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LOW VAPOR PRESSURE BRAZE ALLOYS FOR THERMIONIC ENERGY CONVERTERS

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SUMMARY

The evaluation of cesium diode electrode materials called for braze fillers with very low vapor pressures and a wide range of melting points. Binary alloys of low vapor pressure refractory metals ($<10^{-10}$ torr at $1500^{\circ}K$ and $< 10^{-5}$ torr at $2000^{\circ}K$) were chosen to fill this need. These alloys of Th, Zr, Hf, Ru, Nb, Ir, Mo, Ta, Os, Re, and W have reported melting point minima or eutectics from $1510^{\circ}K$ to above $3000^{\circ}K$.

Preliminary data are compiled on the use of several of these braze alloys. Melting points and surface wetting on a Ta base are given. Results of brazing Ir, LaB_6, Nb, Re, W, and Zr-22 wt% ZrO_2 materials into Ta and Nb-1% Zr bases are presented. Current braze usage is summarized.

INTRODUCTION

An important area of thermionics research today is the screening of numerous new electrode materials. To this end, the diminiode, a cesium diode with planar miniature electrodes, guarded collector, and fixed or variable gap was invented (ref. 1). New low vapor pressure braze fillers were needed in order to attach the various electrode materials to the standardized diminiode. A braze filler vapor pressure criterion of less than 10^{-10} torr at $1500^{\circ}K$ and less than 10^{-5} torr at $2000^{\circ}K$ was set to minimize surface contamination of the electrode materials being tested.

The problem of finding suitable low vapor pressure braze fillers for the diminiode problem was thoroughly discussed in reference 2. This study showed that binary eutectics and melting point minima of Th, Zr, Hf, Ru, Nb, Ir, Mo, Ta, Os, Re, and W would meet the exceptionally low vapor pressure criterion and have a range of melting points from $1510^{\circ}K$ to above $3000^{\circ}K$. Reference 2 tabulated the composition and melting or eutectic points for 55 possible braze alloys.

The purpose of this report is to summarize the preliminary results of using several of these low vapor pressure braze alloys.

APPARATUS AND MATERIALS

Melting and brazing tests were performed in a glass vacuum chamber permitting constant visual observation of the sample (see Figure 1). A vacuum of less than 10^{-5} Torr was maintained during the tests. Uniformity of temperature was brought about by the use of small samples (about 2 mm x 2 mm x .1 mm or less) and induction heating.

A manually operated disappearing filament pyrometer with an effective wavelength of 6530 Å was used to measure temperatures. Total accuracy of the pyrometer including the repeatability of individual operators was within 10°C.

In order to measure true temperatures with the optical pyrometer, a perfect black body is needed. An approximation to the ideal was created by drilling a small hole of depth to width ratio 4 or greater into the center of the Ta pedestal. The emissivity of this cavity was approximately .95 (ref. 3). Brightness corrections using this .95 figure were added to the pyrometer readings to give the true temperatures (ref. 4).

The temperature measurement cavity was used for all of the melting point determinations on a Ta base. Error in this case is due to calibration and repeatability and should be about 10°C. Brazing temperatures were generally measured without a black body cavity. Errors in this case are expected to be an order of magnitude greater.

Sample preparation was found to be very important in the testing and use of these braze alloys. Initial results using alloys made from hot-press sintered powder were poor. The material was inhomogeneous showing a wide range of melting points. Gaseous voids, surface scum, and a general nonmetallic appearance was seen after melting. Appendix A tabulates microhardness values for braze samples used. For Hf-10 Ir and Zr -31.1 Mo, an increase of 130 to 185 kg/mm^2 can be seen in the Knoop hardness number due to increased impurity levels. The Hf-10 Ir hot-press sintered material had 960 ppm oxygen included. As a result, testing was limited to arc-melted samples[1] with non-powder ingredients preferred.

Appendix A lists the actual braze alloy compositions as determined by wet chemical analysis. Compositions were within 2% of nominal except for Zr-10.3 W and Nb-62.9 Ir.

[1]The majority of these were prepared at Lewis Research Center by the Materials Development Section of the Materials and Structures Division.

All braze samples were washed in nitric acid solution to remove surface contamination before brazing. In the case of some of the harder brazes, such as Hf, -18 wt% Ir, several mils of surface was abraded to remove saw cut contamination which could increase the melting point by as much as 200°C.

TESTS AND RESULTS

Melting Point Determinations on Ta Pedestal

Procedure

Using the above apparatus, the sample and Ta pedestal were heated to about 100°C below the melting point and held there for several minutes. The temperature was then increased at about 5°C/min (in 10° jumps) until melting occurred. For the arc-melted materials, the melting point was generally instantaneous due to the small sample size and the eutectic nature of most of the alloys. Samples were visually examined after cool-down for evidence of melting, voids, contamination, etc.

Results

Table I lists the results of melting the braze materials on a Ta pedestal. In all cases our effective melting points were higher than the literature values. As mentioned above, the pyrometer accuracy should be within 10°C. The braze temperature may be lower than the Ta base temperature due to poor thermal contact and surface radiation losses. Other possible sources of discrepancy in results are differences in sample composition and preparation, reactions with the Ta surface and superheating past the eutectic point.

Surface wetting was coded following the method used in a very systematic guide to high-temperature brazes by Cappelletti (ref. 5). Both the wetting and melting point temperature of a braze can change with various bases. This study also found the melting point for Zr-22 Nb. Cappelletti reported 1800°C, fair wetting on a Ta base while we found variable temperatures from 1730°C to 1850°C also with fair wetting. This range may be due to sample inhomogeneity on our part. However, other factors may make this a particularly sensitive braze since Cappelletti has a range of melting points from 1700°C (very good wetting) for Re, 1740°C (fair) for Nb and (good) Mo, to 1800°C (fair) for Ta.

The Ta-46 wt% Ir braze exhibited an attack on the Ta pedestal along with an elevated melting point. This reaction with the base is probably a major cause of the increase in melting point. Tantalum diffusion with the braze alloy would have created a non-eutectic composition and elevated the melting point. Any reactions that were already occurring would have been further intensified with this increase in temperature.

Brazing Trials

Procedure

As with the melting trials the pieces to be joined by brazing were held at a temperature about 100°C below the brazing temperature for several minutes. The rate of heating was generally greater past this point due to a desire to minimize reactions. The brazing temperature was determined when the brightness of the electrode thermal emission increased showing the creation of intimate thermal contact due to the melting of the braze. After cooldown the joint was examined for wetting, reactions, qualitative strength, etc.

Results

Table II summarizes the brazing trial data. Brazing temperatures for several brazes are lower than their melting points on tantalum from Table I (listed again in the second column on Table II). This could be due to the electrode material on top of the braze acting as a radiation shield. Temperature sightings of the base would generally be lower than the true temperature because most of them were not taken from a black body cavity.

Many trials were made with Ta-46 Ir and Zr-22.8 Ru as these were for some time the only low vapor pressure braze fillers used. In order to braze LaB_6, many braze alloys were tested. The best at this time is Zr-31.1 Mo. At high temperatures (> 1500°C) the joint formed by this material was destroyed. A large portion of the LaB_6 electrode near the braze became discolored, due to either reactions with the braze or gas evolution from the hot-press sintered LaB_6.

Prior to the confirmation of Zr-31.1 Mo, Pt was tested as an LaB_6 braze and seemed to work well. It does not meet the low vapor pressure criterion mentioned in the Introduction, however, and so was not used (ref. 6).

The exact form of the braze, electrode, and base materials are given as it is expected that these are important features. The current choice of brazes for use in cesium diodes at our laboratory is given in the far right column on Table II.

CONCLUDING REMARKS

Thermionic cesium diode electrode screening programs call for new low vapor pressure braze alloys. Preliminary results on the use of several of these new alloys is given.

Preferred braze alloys for various materials are Zr-22.8 wt% Ru (brazing point ~ 1290°C) for LaB_6, Nb, Re, Ir, and Zr-22 ZrO_2 on a Nb-1 Zr base; Ta-46 Ir (~ 2000°C) for Re and W on a Ta base; Zr-24.9 Re (~ 1600°C) for Zr-22 ZrO on a Ta base; Zr-31.1 Mo (1560°C) for LaB_6 on a Ta base; pure Ru (~ 1800°C) for Ir on a Ta base.

Lanthanum hexaboride tends to react with most brazes. Platinum tends to wick around the LaB_6 at 1500°C and does not have a very low vapor pressure. At temperatures greater than 1500°C, LaB_6 destructively reacts with the Zr-31 Mo braze.

An unexpected occurrence was the gradual destruction of a seemingly good joint formed with Zr-24.9 Re braze between Ir and Ta. Apparently, a low melting point (~ 1300°C, suspected) Zr-Ir eutectic exists. This may be inferred from the literature by analogy to the Hf-18 Ir eutectic at 1505°C since a Zr-24.9 Re eutectic exists at 1685°C and an Hf-24.3 Re eutectic at 1960°C. Future testing will include longer time at temperature as well as a pre-screening using the fact that Zr and Hf, Nb and Ta, and Mo and W are quite similar in chemical behavior so that unreported eutectics may be inferred from current limited data.

Arc-melted materials, in general, were found to be superior to hot-press sintered materials.

REFERENCES

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5. Cappelletti, C.: Laboratory Guide for the Selection of Brazing Materials. EUR 4637e Commission of the European Communities, 1971.

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TABLE I - EXPERIMENTAL MELTING POINT AND SURFACE WETTING OF Ta BY LOW VAPOR PRESSURE REFRACTORY METAL BRAZE ALLOYS

BRAZING ALLOY WT. % (a)	LITERATURE MELTING POINT °C	EXPERIMENTAL MELTING POINT °C	SURFACE WETTING CODE (b)	COMMENTS
Zr-22.8 Ru	1240	1300	2	
Hf-18 Ir	1430	1505	3	Materials must be very clean for wetting to occur.
Zr-31.1 Mo	1520	1630	1	
Zr-24.9 Re	1600	1685	1	
Zr-18.3 W	1660	1870	1	
Zr-22 Nb	1745	1730, 1850	~3	Variable results
Nb-62.9 Ir	1840	1815, 2145	~3	Variable results
Hf-24.3 Re	1840	1960	2	~.1 mm size voids present
Ta-46 Ir	1950	2155, 2265	1	Variable results Dissolves into Ta

(a) All alloys are formed by arc-melting. All but Zr-22.1 Nb are eutectics.

(b) Wetting code (see ref. 5).

1. 0^{o} wetting angle. Very good flow.
2. Close to 0^{o} wetting angle. Good flow.
3. $0^{o} <$ wetting angle $< 45^{o}$. Fair flow.
4. $45^{o} <$ wetting angle $\leq 90^{o}$. Poor flow.
5. Wetting angle $> 90^{o}$. No flow.

TABLE II - SUMMARY OF BRAZING DATA FOR LOW VAPOR PRESSURE BRAZE ALLOYS

BRAZING ALLOY WT. % (a)	MELTING POINT ON Ta °C	APPARENT BRAZING °C (b)	BASE MATERIAL	ELECTRODE MATERIAL (c)	JOINT QUALITY	PREFERRED FOR DIODE?
		1270	Nb-1 Zr	Ir Crystal	Good.	Yes
		1295	Nb-1 Zr	LaB_6 H.P.S.	Fair.	Yes
		-	Nb-1 Zr	Nb P. Crystal	Good.	Yes
Zr-22.8 Ru	1290	-	Nb-1 Zr	Nb Crystal	Good.	Yes
		1260	Nb-1 Zr	Re Crystal	Very good.	Yes
		1250	Nb-1 Zr	Zr-22 ZrO_2 A.M.	Very good.	Yes
		1290	Ta	LaB_6 H.P.S.	LaB_6 cracked on cycling.	No
		1260+	Ta	W	-	No
Hf-18 Ir	1500	1520+	Ta	LaB_6 H.P.S.	Poor LaB_6 wetting	No
Zr-31.1 Mo	1620	1560+	Ta	LaB_6 H.P.S.	Very good flow on Ta. Fair on LaB_6. Joint destroyed if go above brazing temperature.	Yes
Zr-24.9 Re	1680	1500	Ta	Ir Crystal	Poor. Reacts with Ir.	No
		1620	Ta	Zr-22 ZrO_2 A.M.	Good, if use excess of braze.	Yes
Pt.	1725	1450	Ta	LaB_6 H.P.S.	Wets but wicks into and over LaB_6 during 1500°C operation.	No
Zr-18.3 W	1870	1800+	Ta	LaB_6 A.M.	Poor. Reacts with LaB_6.	No
		1960	Ta	Ir Crystal	Very bad. Dissolves Ir and Ta	No
		-	Ta	Re Crystal	Good.	Yes
Ta-46 Ir	2200	1780	Ta	Zr-22 ZrO_2 A.M.	Bad. Dissolves Ta, Zr-22 ZrO_2	No
		-	Ta	W Crystal	Good.	Yes
		-	Ta	W. V.D.W.	Good.	Yes
Zr		1725	Ta	LaB_6 H.P.S.	Poor. Reacts with LaB_6.	No
Ru		1800	Ta	Ir Crystal	Good.	Yes

(a) All alloys are arc melted and of eutectic composition.

(b) Uncorrected brightness temperature of base surface (+Used black body cavity).

(c) P. crystal = polycrystalline
H.P.S. = hot-press sintered
V.D.W. = vapor deposited wafer
A.M. = arc melted

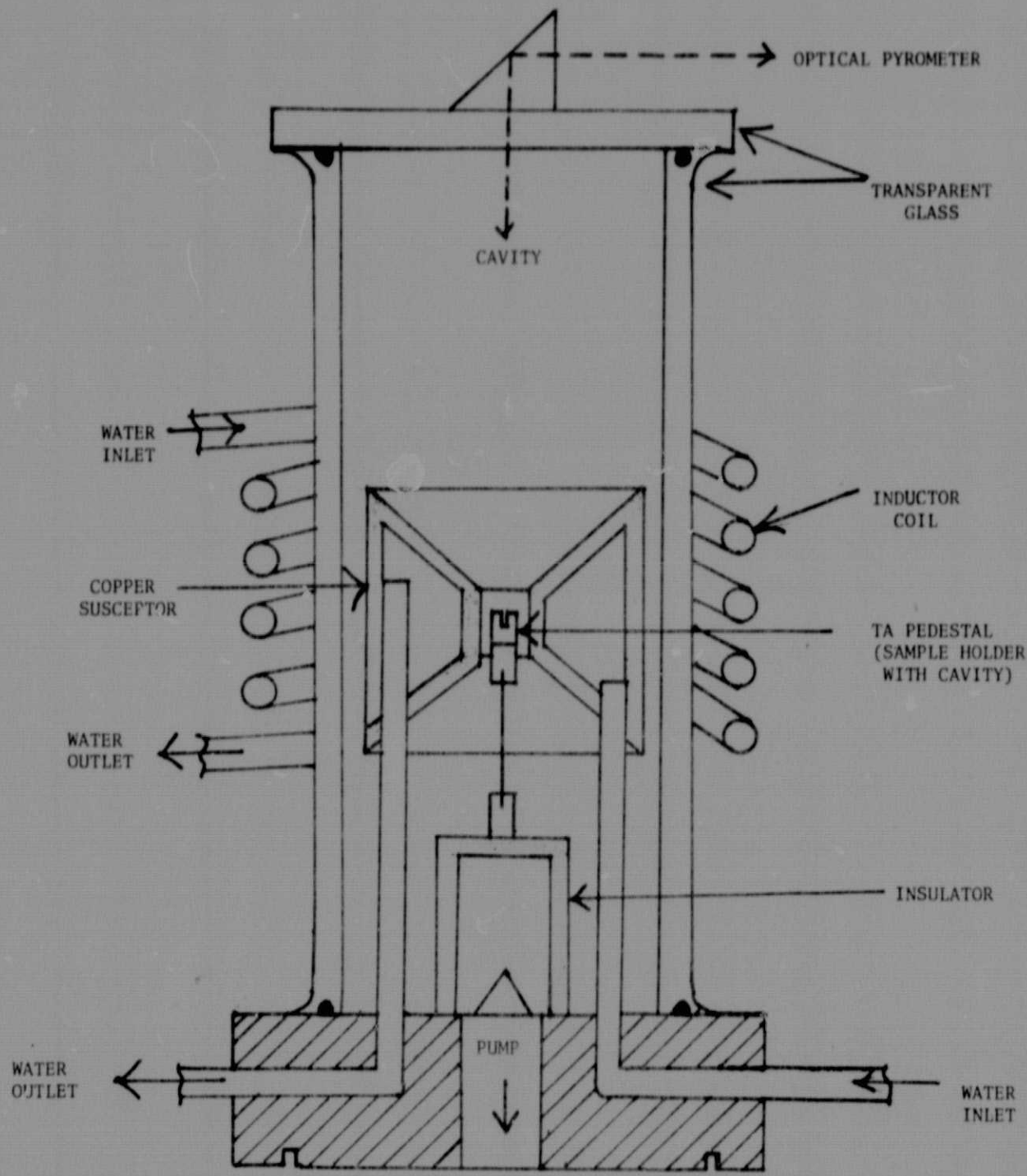
APPENDIX A

KNOOP MICROHARDNESS AND COMPOSITION ANALYSIS FOR BRAZE MATERIALS USED

NOMINAL COMPOSITION	QUANTITATIVE (WET CHEMICAL) ANALYSIS	KNOOP MICROHARDNESS[+] kg/mm^2 (200 g LOAD)
Zr-22.8 Ru	21.7 Ru	400
Hf-18.0 IrA	16.9 Ir	505
Hf-18.0 IrB[*]	17.6 Ir	690
Zr-31.1 MoA	31.5 Mo	405
Zr-31.1 MoB[*]	-	535
Zr-24.9 Re	24.0 Re	390
Zr-18.3 W	13.0 W	425
Zr-22.0 Nb	22.3 Nb	205
Nb-62.9 Ir	51.7 Ir	910
Hf-24.3 Re	25.3 Re	720
Ta-46.0 Ir	-	930

[*]Made by hot-press sintering powder, the rest are arc-melted from bulk metal.

[+]Average value for a limited number of indentations. Actual values ranged from ± 10 to ± 80 kg/mm^2. Typical range was ± 30 kg/mm^2.



MELTING POINT APPARATUS